

Requested Patent: EP1117502A1

Title: WELDING METHOD ;

Abstracted Patent: WO0020157 ;

Publication Date: 2000-04-13 ;

Inventor(s): JONES IAN ANTHONY (GB); WISE ROGER JEREMY (GB) ;

Applicant(s):

JONES IAN ANTHONY (GB); WISE ROGER JEREMY (GB); WELDING INST (GB) ;

Application Number: WO1999GB03241 19990930 ;

Priority Number(s): GB19980021375 19981001 ;

IPC Classification: B23K26/00 ;

Equivalents:

AU6108199, AU749978, BR9914171, CA2345991, CN1139477C, DE69904844D,
DE69904844T, DK1117502T, ES2190660T, JP2002526261T ;

ABSTRACT:

A method of forming a weld between workpieces (1, 2) over a joint region (3). The method comprises: exposing the joint region (3) to incident radiation (4) having a wavelength outside the visible range so as to cause melting of the surface of one or both workpieces at the joint region, and allowing the melted material to cool thereby welding the workpieces together. A radiation absorbing material is provided at the joint region (3) in one of the workpieces (1,2) or between the workpieces which has an absorption band matched to the wavelength of the incident radiation so as to absorb the incident radiation and generate heat for the melting process. The absorption band lies outside the visible range so that the material does not affect the appearance of the joint region (3) or the workpieces (1, 2) in visible light.

S/N 10/822,861
Group 3742
Pg 14



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B23K 26/00	A1	(11) International Publication Number: WO 00/20157 (43) International Publication Date: 13 April 2000 (13.04.00)
--	----	---

(21) International Application Number: PCT/GB99/03241

(22) International Filing Date: 30 September 1999 (30.09.99)

(30) Priority Data:
9821375.4 1 October 1998 (01.10.98) GB(71) Applicant (for all designated States except US): THE WELD-
ING INSTITUTE [GB/GB]; Granta Park, Great Abington,
Cambridge CB1 6AL (GB).

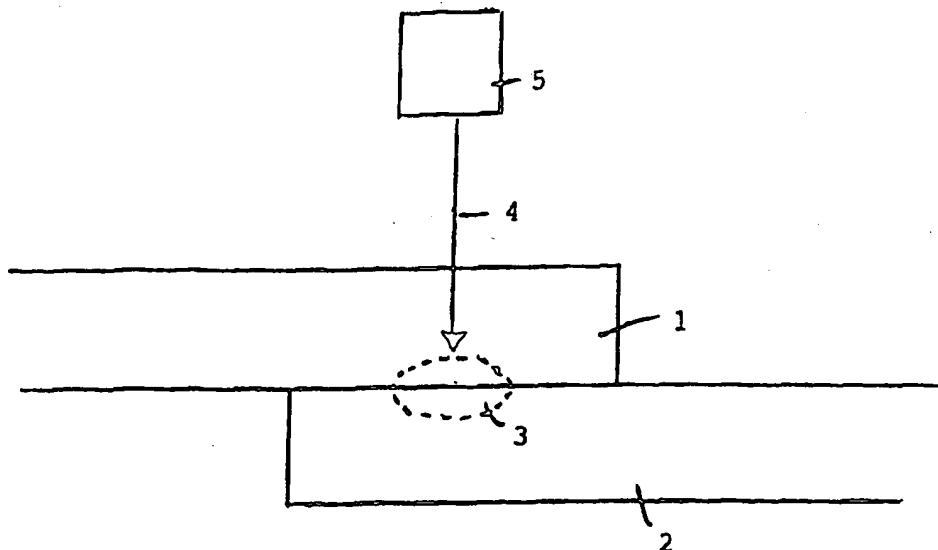
(72) Inventors; and

(75) Inventors/Applicants (for US only): JONES, Ian, Anthony
[GB/GB]; Bardsfield Cottage, Hadstock, Cambridge CB1
6NX (GB). WISE, Roger, Jeremy [GB/GB]; 130 Exning
Road, Newmarket (GB).(74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7
Eldon Street, London EC2M 7LH (GB).(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG,
BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE,
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD,
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD,
SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US,
UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS,
MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: WELDING METHOD



(57) Abstract

A method of forming a weld between workpieces (1, 2) over a joint region (3). The method comprises: exposing the joint region (3) to incident radiation (4) having a wavelength outside the visible range so as to cause melting of the surface of one or both workpieces at the joint region, and allowing the melted material to cool thereby welding the workpieces together. A radiation absorbing material is provided at the joint region (3) in one of the workpieces (1,2) or between the workpieces which has an absorption band matched to the wavelength of the incident radiation so as to absorb the incident radiation and generate heat for the melting process. The absorption band lies outside the visible range so that the material does not affect the appearance of the joint region (3) or the workpieces (1, 2) in visible light.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

WELDING METHOD

The present invention relates to a method of forming
5 a weld between two workpieces, over a joint region.

Transmission laser welding is a technique which has
been developed for welding together materials such as
plastics. This is achieved by positioning two plastic
members in contact, one of which is transparent, the other
10 of which is opaque to visible light. The region of contact
between the two plastic members is then exposed to a laser
beam. The laser beam passes through the transparent
plastic member and is absorbed by the second opaque plastic
member. This causes the opaque plastic member to heat up
15 causing the region of contact between the two plastic
members to melt, thereby forming a weld. Examples are
described in "Laser-transmission welding of PE-HD",
Kunststoffe 87 (1997) 3, pp 348-350; Puetz H et al, "Laser
welding offers array of assembly advantages", Modern
20 Plastics International, September 1997; Haensch D et al,
"Joining hard and soft plastics with a diode laser",
Kunststoffe 88 (1998) 2, pp 210-212; and Jones I A,
"Transmission laser welding of plastics", Bulletin of The
Welding Institute, May/June 1998.

25 All these methods are limited by the need to provide
at least one workpiece which is opaque to visible light.

In accordance with the present invention, we provide
a method of forming a weld between workpieces over a joint
region, the method comprising exposing the joint region to
30 incident radiation having a wavelength outside the visible
range so as to cause melting of the surface of one or both
workpieces at the joint region, and allowing the melted
material to cool thereby welding the workpieces together,
the method further comprising providing a radiation
35 absorbing material at the joint region in one of the
workpieces or between the workpieces which has an
absorption band matched to the wavelength of the incident

radiation so as to absorb the incident radiation and generate heat for the melting process, the absorption band being substantially outside the visible range so that the material does not affect the appearance of the joint region or the workpieces in visible light.

Accordingly, we provide a method for welding workpieces so as to produce a visually transmissive weld. This is achieved by including visually transmissive material at the joint region which absorbs radiation outside the visible spectrum. The joint region is then exposed to radiation of this wavelength, causing the joint region to heat up. This in turn causes the workpieces to melt such that a weld is formed between the two workpieces. If the workpieces and the joint region are themselves transmissive to visible radiation, the weld is also at least translucent to the naked eye.

The workpieces may be opaque and have similar or dissimilar colours and/or be transparent or translucent to visible light.

In some cases, the material absorbent to the radiation is included in one of the workpieces.

In other cases, two workpieces may be welded together with the material being sandwiched between the two workpieces. This then enables workpieces which do not include a suitable radiation absorbing material to be welded together.

The radiation absorbing materials, which are typically in the form of additives, may comprise dyes or pigments while the use of an additive allows standard plastics and other materials to be readily modified to allow welding by the new method. Dyes are preferred to pigments because the particulate nature of pigments means that light scattering occurs and light absorption efficiency is reduced. In addition the low molar absorption coefficients of pigments means that higher concentrations have to be used to produce a given heating effect, and apart from the cost disadvantages, this can lead to undesirable changes in the

physical properties of the host, including the appearance of unwanted colour. In the remainder of this specification, dyes will be referred to although the alternative of pigments may also be appropriate.

5 In some cases the radiation absorbing material may have some residual colour that is visible when viewed as thick sections or with high concentrations of the material present. The strongest absorption will always be in invisible regions, however.

10 An ideal near-infrared dye for laser welding of transparent plastics would have the following attributes:

- A narrow, absorption band near 800nm, (or longer wavelengths, depending on the laser used) with a high molar absorption coefficient.
- 15 • Little if any absorption in the region 400-700nm.
- Good solubility in the host.
- Good stability towards the incorporation method used.
- Should not degrade to coloured by-products.

20

Examples of three dye types which can satisfy all of the above requirements are the cyanine dyes, the squarylium dyes, and the croconium dyes.

Each of the workpieces will typically be made of
25 plastics material although these need not be the same. An example is PMMA perspex. The radiation absorbing material may be provided in just one of the workpieces or in an insert to be placed between the workpieces.

Near infrared absorber dyes have the properties of
30 absorbing light in the region beyond 780nm with high efficiency. That is, they have high extinction coefficients at one or many wavelengths in that spectral region. When this light is absorbed whether it be from a laser source or an incoherent light source, the molecules dissipate the
35 absorbed energy principally as heat via vibronic relaxations, and this heat is localised to the dye molecules and to their immediate host environment. In the

case where the host is a polymer (most thermoplastics and some highly crosslinked polymers as well), a melting occurs at the surface where the dye and polymer are. If a clear polymer (i.e., one that does not absorb NIR radiation but which may simultaneously be water white or coloured) is adjacent to this surface, the melting will cause a weld to occur.

Thus, in order to have the weld occur, the dye must be absent from the front plastic entity allowing the laser light to pass through it unabsorbed and must be localised at least at the surface of the other plastic entity or at the interface between the two plastic pieces. In this sense, the lamina of dye is essentially behaving as an optical focal element for the laser light, absorbing it very efficiently in an extremely thin layer and converting the absorbed light to heat in that same layer. The laser light as well as other wavelengths of light are otherwise effectively transmitted by the remainder of the ensemble which lies in front of this laminar surface as well as behind this surface (an exception to the latter is when the option is used in which one element to be welded has its bulk pervaded by the dye). The establishment of such a dye-laden laminar surface can be accomplished in several ways:

- The dye can be incorporated into a thin film which can be placed at the interface of the plastic pieces to be welded. The film substrate can be the same polymer(s) being welded but may also be a different polymer. Dye concentrations of approximately 0.02% on a film weight basis are typically adequate but are a function of the particular dye used as well as the plastics being welded. A film thickness of approximately 25 μ m is also typical. The advantage of using a film/tape containing the absorber dye is that the dye is needed in the film only where there is to be welding and its

carrier is a solid allowing for ease of handling, storage, etc. Another advantage is that both plastic pieces can be of the same material and may notably be transparent plastic.

- 5 • The dye can be introduced into the bulk of the polymer of the latter of the two polymer pieces (latter in terms of which one the laser light encounters). Only that dye at or very near the surface is active at absorbing the laser light
- 10 since the dyes are highly efficient NIR absorbers. The light absorption results in the weld as before but without the use of tape/film. The advantage is that there is no extra step in the welding manufacturing having to do with
- 15 application of tape, etc.
- The surface of the latter plastic piece can be made, for instance, by having a dye laden film used as a mould insert in a moulding operation to generate the dye rich surface on the plastic
- 20 piece.
- The surface of one of the substrates to be moulded may be imparted a surface application of the dye by dip coating, dye infusion, painting, spraying, printing, dry burnishing, paste
- 25 application, etc. This is a low cost alternative in terms of dye used and offers flexibility in that only selected areas can be treated.
- The material to be welded can be coextruded with polymer containing the dye, but this can
- 30 restrict the approach to certain applications able to make use of the extruded form.
- A plastic piece can be overmoulded to provide a narrow strip, for example, to a selected area, but this encounters a higher moulding cost.

35

The radiation absorbing material could be exposed directly to the radiation and then the two pieces butted

together (optionally under pressure) or more usually will be exposed through a workpiece. Typically, that workpiece will not include a radiation absorbing material so that heating is localised to the interface between the two workpieces.

Typically, the radiation having the predetermined wavelength is infrared radiation, for example with a wavelength of substantially 780nm or more, typically up to 1500nm. It will however be realised that any radiation outside the visible spectrum may be used providing a suitable radiation absorbing material is available, and, if appropriate, one side of the joint is transmissive to the radiation used.

A variety of conventional radiation sources may be used including both diode and Nd:YAG lasers. Focused infrared lamps could also be used.

Examples of methods according to the present invention will now be described with reference to the accompanying drawings, in which:-

Figures 1 to 3 are schematic side views of three different welds.

Figure 1 shows a first plastics workpiece 1 and a second plastics workpiece 2 positioned in overlapping contact so as to define a joint region indicated at 3. The joint is welded by exposing the joint region 3 to a beam of non-visible radiation 4 from a source such as a laser 5, an i.r. lamp or the like.

The first plastics workpiece 1 is transmissive to radiation from the radiation beam 4 and may or may not transmit visible light. In this respect, transmissive means that the plastics workpiece 1 absorbs less than a predetermined portion of the incident radiation. Accordingly, the plastics workpiece 1 may be transparent or translucent to radiation in the visible spectrum, or may reflect such radiation but typically will not be totally absorbent (ie. black). Thus, the plastics workpiece 1

will be either colourless, clear with a coloured tint, or coloured.

The plastics workpiece 2 also may or may not be transmissive to radiation in the visible spectrum. However, in contrast to the plastics workpiece 1, it is necessary for the plastics workpiece 2 to be able to absorb the radiation beam 4. Accordingly, an additive is added to the plastics workpiece 2, the additive being absorptive of the radiation beam wavelength and being transmissive to radiation in the visible spectrum. Because only the joint region 3 will be exposed to the radiation beam 4, the additive may be provided only in the part of the plastics workpiece 2 which is to form the joint region, or alternatively it may be provided throughout the entire plastics workpiece 2.

The radiation beam 4 has a wavelength outside the visible spectrum but in a range which will be absorbed by the additive. This is typically infrared radiation having a wavelength between 780-1500nm. Accordingly, the laser 5 may be an Nd:YAG laser, or a diode laser.

When the joint region 3 is exposed to the radiation beam 4, the additive will absorb the radiation. This causes the additive to heat up melting the plastics workpieces 1,2 in the joint region 3, whereby on cooling the workpieces weld together. When the weld is formed, because the materials at the weld are transmissive to radiation in the visible spectrum, the weld itself will make little or no change to the visible appearance of the component. Welding occurs as a result of the heat generated giving melting of the plastic material up to a depth of typically 0.2mm. Where compatible material is in good contact interdiffusion of molecules and hence welding will occur. The heat generation at the weld interface is controlled by the absorption coefficient of the dye layer, and the processing parameters. The main parameters are laser power, which is typically between 10W and 500W, the welding speed (typically 5-200mm/sec) and the spot size of

the laser beam (0.5-10mm wide). Processing can also be carried out with a fixed laser array, which would irradiate the joint area for a defined time.

A second embodiment of the present invention is shown in Figure 2. In Figure 2, there is provided a first plastics workpiece 11 and a second plastics workpiece 12. There is also provided a thin film of weld material 16 which is positioned between the first plastics workpiece 11 and the second plastics workpiece 12, so as to define a joint region 13. In order to weld the first and second plastics workpieces 11,12, the joint region 13 is exposed to the beam of radiation 14, from a source 15 such as a laser or the like.

As in the first embodiment of the present invention, the first and second plastics workpieces 11,12 may or may not be transmissive to radiation in the visible spectrum. However, in contrast to the first embodiment, it is not necessary for the second plastics workpiece 12 to absorb the radiation from the radiation beam 14.

However, the weld film 16 whilst being transmissive to radiation in the visible spectrum is absorptive to radiation from the radiation beam 14. Thus, as in the first embodiment of the present invention, when the joint region 13 is exposed to the radiation beam 14, the weld material 16 absorbs heat causing heating of the surrounding joint region 3. Consequently the plastics workpieces 11,12 melt in the joint region 13 and on cooling form a weld. Again this is optically transmissive to radiation in the visible spectrum.

In its most basic form absorption in a translucent material follows an exponential link to thickness (ignoring the effects of reflection and scattering), i.e.

$$\text{fraction transmitted} = \exp(-at)$$

where a is the absorption coefficient and t is the thickness of the workpiece. The absorption coefficients

for the translucent plastics we have measured range from 0.02mm^{-1} to 0.4mm^{-1} at 800-1100nm wavelength. Thus a useful range is anything less than about 1mm^{-1} for a translucent plastic. In a process of the form shown in Figure 2, the layer of dye had an absorption coefficient of about 5.4mm^{-1} . Typically, therefore, the absorptive layer should have an absorption coefficient greater than about 3mm^{-1} .

It will be realised that in either of the above examples, the plastics workpieces 1,2; 11,12 may be clamped together during the welding process to ensure the joint region is maintained in contact while the weld forms. Alternatively, the component with the absorptive material may be irradiated first and then the workpieces brought together.

A further weld configuration is shown in Figure 3 in which a pair of plastics workpieces 20,21 are welded together using a transparent insert 22 which is absorbent to laser light. The workpieces 20,21 in this case are not absorbent to laser light.

It will be appreciated that many further variations are possible such as butt welds and the like.

Typical absorbent additives can be selected from chemical groups such as metal phthalocyanine dyes, metalated azo dyes and metalated indoaniline dyes. Table 1 below provides a set of examples of matched sources and materials:

Table 1

Light source	Wavelength range nm	Absorbing medium	Wavelength range nm
Infrared lamp	700-2500	Gentex dye A195 Gentex dye A101	780-1100 750-1100
Nd:YAG laser	1064	Gentex dye A195	780-1100
Diode laser, GaAs	940-980	Gentex dye A195	780-1100
Diode laser, InGaAs	790-860	Gentex dye A187	821-858

Examples

PMMA sheet welding: Two clear sheets of polymethylmethacrylate approximately 3mm thick have been lap welded using the ClearWeld™ process with a Nd:YAG laser. A 10-15µm MMA film containing typically 0.01-0.1wt% infrared absorbing dye was placed at the interface. The two pieces were clamped together and welded with an applied power of 100W at speeds in the range 0.1-1.0m/min. The laser beam used was approximately 6mm in diameter and the film was 5mm wide. Tensile tests on these samples gave failure in the parent material adjacent to the weld with loads in the order of 50N/mm. The weld obtained had very little residual colour and was as clear or clearer than the parent PMMA.

15 Polyurethane coated fabric welding: Two white translucent pieces of polyurethane coated fabric approximately 0.15mm thick have been lap welded using the ClearWeld™ process. The infrared absorbing dye was applied from solution in acetone to the region to be welded between the lapped pieces. Typically 0.001-0.1µg/mm² of dye were applied to the fabric. The two pieces were clamped together and welded with an applied power of 100W at speeds in the range 0.5-2.0m/min. The laser beam used was approximately 6mm in diameter. The weld obtained had very little residual colour.

30 PA/PTFE laminate fabric welding: Two coloured opaque pieces of polyamide/polytetrafluoroethylene laminated fabric approximately 0.15mm thick have been lap welded using the ClearWeld™ process. The infrared absorbing dye was applied from solution in acetone to the region to be welded between the lapped pieces. Typically 0.001-0.1µg/mm² of dye were applied to the fabric. The two pieces were clamped together and welded with an applied power of 100W at speeds in the range 0.1-1.0m/min. The laser beam used was approximately 6mm in diameter. The weld region

obtained had no apparent residual colour apart from that of the original fabric.

The welding technique has also been used for welding nylon based fabrics (laser stitching/sewing/seam-sealing/etc.) and thin films (PE, PEEK). In these cases the dye was dissolved in a suitable solvent and painted over the joint region with resultant deposition of dye both at the surface and infusion of dye very slightly into the substrate. It was allowed to dry prior to welding. Clearly, use of polymeric substrates such as polyester, polycarbonate, polystyrene, polysilicones, etc. either alone or in textile or other blends and numerous thermoplastic films are obvious extensions of this example. It should be noted that while maximum dye utility is attained when the dye is truly dissolved in the substrate (film or bulk or other carrier), suspensions of dye applied in these modes are also efficient for the welding applications described above.

CLAIMS

1. A method of forming a weld between workpieces over a joint region, the method comprising:
 - 5 exposing the joint region to incident radiation having a wavelength outside the visible range so as to cause melting of the surface of one or both workpieces at the joint region, and allowing the melted material to cool thereby welding the workpieces together, the method further
 - 10 comprising providing a radiation absorbing material at the joint region in one of the workpieces or between the workpieces which has an absorption band matched to the wavelength of the incident radiation so as to absorb the incident radiation and generate heat for the melting
 - 15 process, the absorption band being substantially outside the visible range so that the material does not affect the appearance of the joint region or the workpieces in visible light.
2. A method according to claim 1, wherein the radiation
- 20 absorbing material is sandwiched between two workpieces.
3. A method according to claim 1, wherein the radiation absorbing material is provided in at least one of the workpieces.
4. A method according to claim 1, wherein the radiation
- 25 absorbing material is provided on the substrate by moulding the substrate in a mould with an insert formed by or including the radiation absorbent material.
5. A method according to claim 1, wherein the radiation absorbent material is provided as a coating on the
- 30 substrate.
6. A method according to claim 1, wherein the radiation absorbent material is provided by coextruding the material with the substrate.
7. A method according to any of the preceding claims,
- 35 wherein the radiation absorbing material is exposed to radiation prior to positioning the workpieces together.

8. A method according to any of the preceding claims, wherein the radiation absorbing material is exposed to radiation through one of the workpieces.
9. A method according to any of the preceding claims,
5 wherein the workpieces are made of plastics.
10. A method according to any of the preceding claims, wherein the radiation absorbing material is a radiation absorbing dye.
11. A method according to any of the preceding claims,
10 wherein the lower limit of the absorption band is above 700nm.
12. A method according to claim 11, wherein the absorption band defines the range 780-1100nm.
13. A method according to any of claims 1 to 11, wherein
15 the absorption band defines the range 820-860nm.
14. A method according to any of claims 1 to 11, wherein the absorption band lies in the infrared range.
15. A method according to any of the preceding claims, wherein the absorption band does not include the range 400-
20 700nm.
16. A method according to any of the preceding claims, wherein the radiation is in the infrared range.
17. A method according to any of the preceding claims, wherein the wavelength of the incident radiation lies in
25 the range 700-2500nm.
18. A method according to claim 17, wherein the wavelength of the incident radiation lies in the range 790-860nm.
19. A method according to claim 17, wherein the wavelength of the incident radiation lies in the range 940-980nm.
- 30 20. A method according to any of the preceding claims, wherein the radiation is a laser beam.
21. A pair of workpieces which have been welded by a method according to any of the preceding claims.

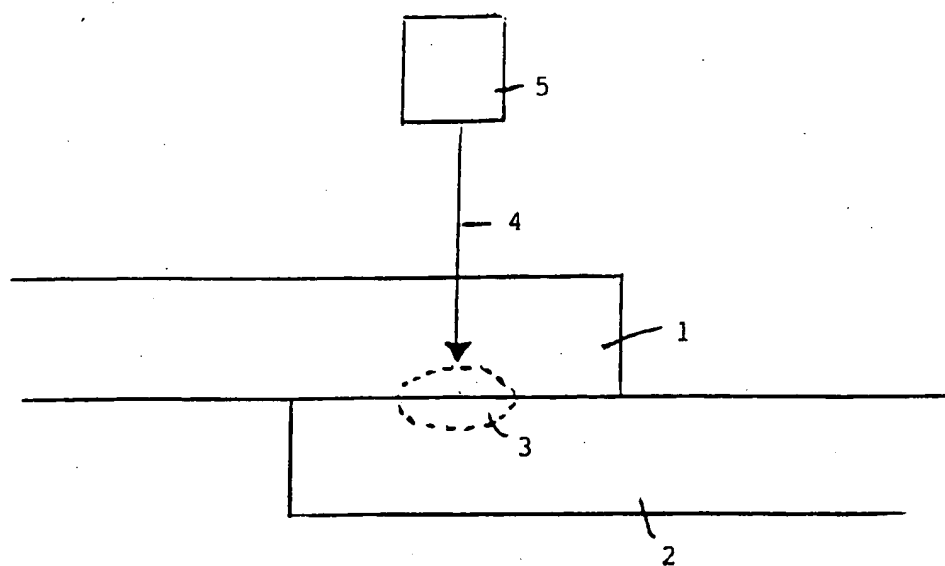


FIGURE 1

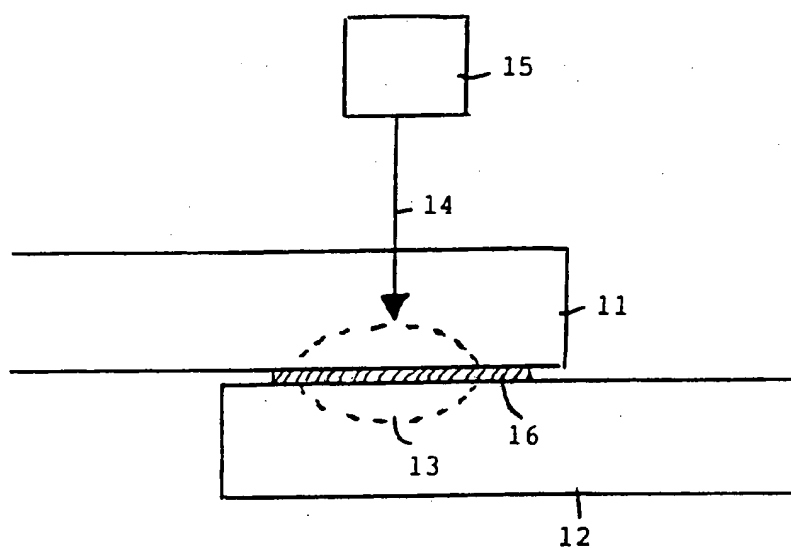


FIGURE 2

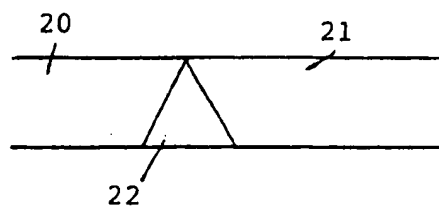


FIGURE 3

INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/GB 99/03241

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B23K26/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):
IPC 7 B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 282 181 A (IMPERIAL CHEMICAL INDUSTRIES PLC) 14 September 1988 (1988-09-14) page 3, line 46 - line 52 ----	1, 3, 9, 11-15, 17-21
A	US 4 606 859 A (DAGGAN ET AL.) 19 August 1986 (1986-08-19) column 6, line 27 - line 42 -----	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 January 2000

Date of mailing of the international search report

19/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Herbreteau, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat . Application No

PCT/GB 99/03241

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0282181	A	14-09-1988	AT 113978 T	15-11-1994
			AU 1212788 A	08-09-1988
			CA 1330435 A	28-06-1994
			DE 3852050 D	15-12-1994
			DE 3852050 T	06-04-1995
			JP 2614890 B	28-05-1997
			JP 63308073 A	15-12-1988
			KR 9601062 B	18-01-1996
			US 4824947 A	25-04-1989
<hr/>				
US 4606859	A	19-08-1986	AT 51402 T	15-04-1990
			BR 8501253 A	12-11-1985
			EP 0155780 A	25-09-1985
			HK 65390 A	31-08-1990
			JP 2012921 C	02-02-1996
			JP 4075916 B	02-12-1992
			JP 60209583 A	22-10-1985
			KR 9400369 B	19-01-1994
			PH 21552 A	11-12-1987
			SG 45490 G	17-08-1990
<hr/>				